Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Potassium bis(ethylenediamine)-copper(II) ferricyanide

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Received 9 April 1999
Accepted 26 July 1999

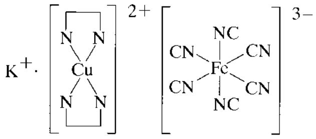
The title compound, potassium bis(ethylenediamine-*N*,*N'*)copper(II) hexacyanoferrate(III), $K[Cu(C_2H_8N_2)_2]$-$[Fe(CN)_6]$, contains $[Cu(en)_2]^{2+}$ and $[Fe(CN)_6]^{3-}$ complex ions, where en is ethylenediamine. The Fe^{III} and K^+ ions lie on twofold axes and the Cu^{II} atom lies on an inversion center. The $[Cu(en)_2]^{2+}$ ion has square-planar coordination with a mean Cu—N distance of 1.992 (2) Å and the $[Fe(CN)_6]^{3-}$ ion has distorted octahedral coordination with a mean Fe—C distance of 1.947 (2) Å.

Comment

The crystal engineering of two- and three-dimensional polymers is of current interest not only from the theoretical aspect related to the topologies of novel networks with inner cavities and channels (Hoskins & Robson, 1990; Carlucci *et al.*, 1995; Yaghi & Li, 1995; Black *et al.*, 1996), but also because of the potential applications of such complexes in catalysis (Fujita *et al.*, 1994), host–guest chemistry (Yaghi *et al.*, 1997) and molecular electronics (Fallah *et al.*, 1996; Miyasaka *et al.*, 1996). One of the most successful strategies leading to extended heterometallic supramolecular architecture is the use of metal cations such as Cu^{2+} or its coordinated ions to link relatively stable coordination anions such as $[Fe(CN)_6]^{3-}$ containing potential bridging units, here the cyanide groups. Such synthetic strategy has provided many complexes in the literature with extended networks possessing interesting photochemical, electrochemical and magnetic properties.

Cyanide is an ambidentate ligand capable of simultaneously bridging two metal centers in an asymmetric mode. Although the extended structure of Prussian blue with cyanide C-bonded to low-spin Fe^{II} and N-bonded to high-spin Fe^{III} has been known for a long time (Buser *et al.*, 1977), the cyano-bridged polymeric materials have not received much attention until recently. Prussian blue analogues (Miyasaka *et al.*, 1995; Ohba *et al.*, 1994, 1995; Mallah *et al.*, 1995) derived from the assembly of the anionic block $[M(CN)_6]^{3-}$ (M = Cr, Fe, Mn *etc.*) and the cationic fragment $(M'L_m)^{n+}$ (M' = Cu, Ni, Co, Fe *etc.*; L is a neutral terminal-N-containing ligand; m and n = 1, 2 or 3) having one to four unsaturated coordination sites, are potential molecular-based magnets, some of which are magnetically ordered at high temperature.

Due to the aforementioned interest, we have reacted $[Cu(en)_2]^{2+}$ with $[Fe(CN)_6]^{3-}$ (en is ethylenediamine). However, with a $CuCl_2$:Fe^{III} molar ratio of 1.5:1, in the presence of en, an ionic complex with discrete cations and anions was formed, instead of polymeric coordination complexes with extended networks such as formed with various ratios of $CuBr_2$:Fe^{III} (Zhang, 1999). It is possible that the larger Br^- ion assisted in the network formation. This ionic title complex, (I), contains $[Cu(en)_2]^{2+}$ cations and $[Fe(CN)_6]^{3-}$ anions with one K^+ ion to balance the ionic charge and also template the crystal lattice (Fig. 1). The $[Cu(en)_2]^{2+}$ cation is planar, with Cu^{2+} chelated by two en ligands with an average Cu—N distance of 1.992 (2) Å and an N—Cu—N bite angle of 84.97 (8)°. The $[Fe(CN)_6]^{3-}$ anion is a slightly distorted octahedron with all Fe—C distances nearly equivalent [average 1.947 (2) Å]. However, only one of the *trans*-C—Fe—C angles is close to 180° [C4—Fe—C4($-x$, y, $\frac{1}{2}-z$) 179.48 (10)°], while the other two deviate by 6.55 (6)° from linearity (Fig. 2).



(I)

Each Fe center in the anions is C-bonded to six cyanide ions, which are weakly bound to five different K^+ ions at the nitrogen ends [average K···N 2.84 (3) Å]. The K···N—C—Fe pathways are of two kinds, one is quasi-linear with an average K···N—C angle of 176.1° (Morpurgo *et al.*, 1980, 1981), while

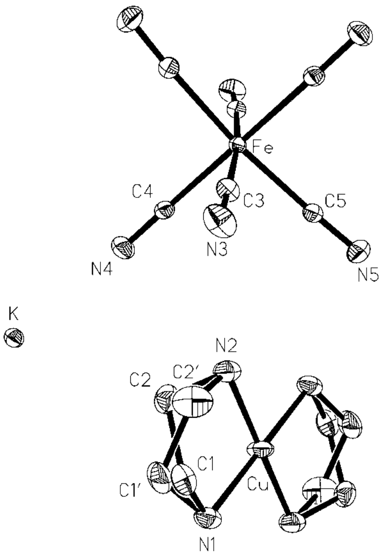


Figure 1
The molecular structure of $K[Cu(en)_2][Fe(CN)_6]$ with displacement ellipsoids at the 30% probability level.

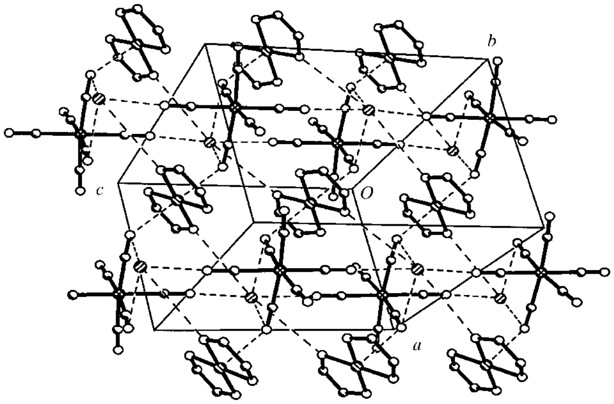


Figure 2
The packing of the cations and anions of $K[Cu(en)_2][Fe(CN)_6]$, showing the weak interactions between K and N, and between Cu and N.

the other is non-linear with an average $K\cdots N—C$ angle of 85.2° (Ibrahim *et al.*, 1998). The $[Cu(en)_2]^{2+}$ cations are thus located diagonally within the loose cubic cavities formed by six $[Fe(CN)_6]^{3-}$ anions through weak $N\cdots K$ interactions, with a $Cu\cdots N5(1-x, y, \frac{1}{2}-z)$ distance of 2.8604 (8) Å.

Experimental

To an aqueous solution (20 ml) containing $K_3[Fe(CN)_6]$ (0.281 g, 1.0 mmol) was added $CuCl_2\cdot 2H_2O$ (0.256 g, 1.5 mmol) with stirring at room temperature, followed by the addition of en (0.180 g, 3.0 mmol). After stirring for 10 min, the resulting dark solution was evaporated at room temperature for a week, giving crystalline plates of the title complex in 60% yield. Analysis calculated for $C_{10}H_{16}CuFeKN_{10}$: C 27.6, H 3.7, N 32.2%; found: C 27.7, H 3.7, N 32.3%.

Crystal data

$K[Cu(C_2H_8N_2)_2][Fe(CN)_6]$
$M_r = 434.82$
Monoclinic, $C2/c$
$a = 8.428$ (1) Å
$b = 16.863$ (1) Å
$c = 11.869$ (1) Å
$\beta = 98.86$ (1)°
$V = 1666.7$ (3) Å^3
$Z = 4$

$D_x = 1.733$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31 reflections
$\theta = 2.98–16.48°$
$\mu = 2.410$ mm^{-1}
$T = 295$ (2) K
Rectangular, black
0.40 × 0.32 × 0.30 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.813$, $T_{max} = 0.921$
2601 measured reflections
2206 independent reflections
1856 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 29°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 22$
$l = -16 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 2.69%

Refinement

Refinement on F^2
$R(F) = 0.027$
$wR(F^2) = 0.068$
$S = 0.966$
2206 reflections
107 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

The C1 and C2 atoms are disordered over two positions and were refined with half occupancies.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*/*PC*.

This work was supported by the NNSF (grant No. 29671035) of the People's Republic of China, the RFDP of Higher Education, and the State Key Laboratory of Coordination Chemistry, Nanjing University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1254). Services for accessing these data are described at the back of the journal.

References

Black, J. R., Champness, N. R., Levason, W. & Reid, G. (1996). *Inorg. Chem.* **35**, 4432–4438.
Buser, H. J., Schwarzenbach, D., Petter, W. & Ludi, A. (1977). *Inorg. Chem.* **16**, 2704–2710.
Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1995). *Inorg. Chem.* **34**, 5698–5700.
Fallah, M. S. E., Rentschler, E., Caneschi, A., Sessoli, R. & Gatteschi, D. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1947–1949.
Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, K (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.
Hoskins, B. F. & Robson, R. (1990). *J. Am. Chem. Soc.* **112**, 1546–1554.
Ibrahim, A. M. A., Siebel, E. & Fischer, R. D. (1998). *Inorg. Chem.* **37**, 3521–3525.
Mallah, T., Auberger, C., Verdaguer, M. & Veillet, P. (1995). *J. Chem. Soc. Chem. Commun.* pp. 61–62.
Miyasaka, H., Matsumoto, N., Okawa, H., Re, N., Gallo, E. & Floriani, C. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1446–1446.
Miyasaka, H., Matsumoto, N., Okawa, H., Re, N., Gallo, E. & Floriani, C. (1996). *J. Am. Chem. Soc.* **118**, 981–994.
Morpurgo, G. O., Mosini, V., Porta, P., Dessy, G. & Fares, V. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1272–1276.
Morpurgo, G. O., Mosini, V., Porta, P., Dessy, G. & Fares, V. (1981). *J. Chem. Soc. Dalton Trans.* pp. 111–117.
North, A. C. T., Philips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ohba, M., Maruono, N., Okawa, H., Enoki, T. & Latour, J. M. (1994). *J. Am. Chem. Soc.* **116**, 11566–11567.
Ohba, M., Okawa, H., Ito, T. & Ohto, A. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1515–1516.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997*a*). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL/PC*. Version 5.101. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *XSCANS. X-ray Single Crystal Analysis Software*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Yaghi, O. M., Davis, C. E., Li, G. M. & Li, H. L. (1997). *J. Am. Chem. Soc.* **119**, 2861–2868.
Yaghi, O. M. & Li, G. M. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 207–209.
Zhang, H.-X. (1999). Unpublished results.

Acta Cryst. (2000). C**56**, 40–41 Bei-Sheng Kang *et al.* • $K[Cu(C_2H_8N_2)_2][Fe(CN)_6]$ **41**